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(54) Title: METHODS FOR ADJUSTING MELT PROPERTIES OF METALLOCENE CATALYZED OLEFIN COPOLYMERS

(57) Abstract: The melt strength and the melt index ratio of ethylene-based polyolefins are controlled by the lower alkyl substitution pattern of the bridged cyclopentadienyl ligands of metallocene polymerization catalyst precursor compounds.

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## **METHODS FOR ADJUSTING MELT PROPERTIES OF METALLOCENE CATALYZED OLEFIN COPOLYMERS**

### **FIELD OF THE INVENTION**

5 [0001] The present invention relates to methods for adjusting melt (viscoelastic) properties of olefin copolymers and preferably ethylene copolymers prepared utilizing bridged metallocene-based catalysts. In particular, the present invention relates to methods for improving (optimizing) the melt strength and controlling the Melt Index Ratio (MIR) of ethylene-based polyolefins.

### **BACKGROUND OF THE INVENTION**

10 [0002] The use of metallocene-based catalysts for the polymerization of olefins is well known. A variety of metallocene catalyst precursor compounds have been shown to be highly useful in the preparation of polyolefins, producing relatively homogeneous copolymers at good  
15 polymerization rates. In contrast to traditional Ziegler-Natta catalyst compositions, metallocene-based catalyst compositions contain one or only a few polymerization sites, thereby allowing one to tailor the properties of the finished polymer closely. However, relatively little is still known as to how individual structural features of metallocene catalyst precursor compounds influence the properties of the polymers produced thereby.

20 [0003] U.S. Patent No. 6,034,192 discloses germanium bridged metallocenes such as, e.g., diethylgermanium cyclopentadienyl tetramethylcyclopentadienyl zirconium dichloride for the production of ethylene polymers with increased melt strength. PCT Patent Application Publication No. WO 99/41294 is directed to a solution polymerization process for the preparation of ethylene copolymers with a catalyst composition prepared from a bridged  
25 bis(cyclopentadienyl) zirconium compound having an unsubstituted cyclopentadienyl ligand and a multiply substituted cyclopentadienyl ligand. The process is stated to exhibit high catalyst activity, high comonomer incorporation and high diene monomer conversion rates and to be particularly suitable for the preparation of ethylene-based elastomers.

30 [0004] In addition, pending U.S. Patent Application, Ser. No. 09/306,142, filed May 6, 1999 discloses cyclic bridged metallocene catalyst systems, their use in a polymerization process, and products produced therefrom. Pending U.S. Patent Application, Ser. No. 09/955,507, filed September 18, 2001, which is a continuation of U.S. Patent Application, Ser.

## DETAILED DESCRIPTION

### Introduction

[0007] The present invention provides for the control and adjustment of certain melt properties, in particular, melt strength and MIR of metallocene-catalyzed ethylene-based polyolefins. Melt strength and MIR are properties which influence the behavior of these polyolefins when they are made into articles such as, e.g., blown film. It has now unexpectedly been found that both of these properties can be optimized and controlled, respectively, by using metallocene catalyst precursor compounds having two cyclopentadienyl ligands connected by a bridging moiety and varying and selecting, respectively, the number of the (lower alkyl) substituents on these cyclopentadienyl ligands.

[0008] For the purposes of this patent specification, the term "catalyst" refers to a metal compound, that when combined with an activator, polymerizes olefins. The term "activator" is used interchangeably with the term "co-catalyst", and the term "catalyst system" refers to the combination of catalyst, activator, and optionally a support material. In addition, unless otherwise stated, all percentages, parts, ratios, etc., are by weight. Also, unless otherwise stated, a reference to a compound or component (e.g., the catalyst precursor compounds used in the method of the present invention) includes the compound or component by itself, any of its individual stereoisomers (e.g., rac and meso) and any mixtures thereof, as well as any combination with other compounds or components, such as mixtures of compounds.

[0009] Further, when an amount, concentration, or other value or parameter, is given as a list of upper preferable values and lower preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of an upper preferred value and a lower preferred value, regardless whether ranges are separately disclosed. Moreover, the upper and lower values of any two or more ranges given for a specific parameter are to be understood as also disclosing the ranges formed by combining the lower value of a first range with the upper value of a second range and *vice versa*.

### Bridged Metallocene-Based Catalyst Compounds

[0010] In the methods of the present invention, the metallocene catalyst compounds utilized contain a metal atom bound to at least one anionic leaving group and also bound to two cyclopentadienyl ligands which are bound together via a bridging group. In one embodiment, the metallocene utilized is represented by Formula I:



Formula I

groups, dienes or a group bonded to M through a nitrogen, phosphorus or oxygen atom. In a preferred embodiment, each Q is selected from chlorine and C<sub>1</sub>-C<sub>4</sub> alkyl groups.

[0016] In another embodiment, the two Q groups may be joined together to form an alkenyl group or a conjugated diene ligand which is coordinated to the metal in a metallocyclopentene fashion; or the two additional ligands may be combined into a conjugated diene which forms a  $\pi$ -complex with the metal atom.

[0017] In a preferred embodiment, each Q is independently halogen, C<sub>1</sub>-C<sub>6</sub> alkyl groups (e.g., methyl and ethyl), C<sub>6</sub>-C<sub>10</sub> aryl groups (e.g., phenyl), C<sub>7</sub>-C<sub>12</sub> arylalkyl groups (e.g., benzyl) and C<sub>7</sub>-C<sub>12</sub> alkylaryl groups (e.g., tolyl).

[0018] Depending on the oxidation state of the M, the value for n is 0, 1 or 2 such that Formula I above represents a neutral metallocene catalyst compound.

[0019] A is a bridging group bonded to L<sup>A</sup> and L<sup>B</sup>. Non-limiting examples of bridging group A include groups containing at least one Group 13 to 16 atom(s), often referred to as a divalent moiety such as but not limited to at least one of a carbon, oxygen, nitrogen, silicon, aluminum, boron, germanium and tin atom or a combination thereof. Preferably bridging group A contains a carbon, silicon or germanium atom. More preferably bridging group A contains at least one silicon atom(s) or at least one carbon atom(s).

[0020] In one embodiment, bridging group A includes radicals comprising at least one Group 14 atom such as carbon, silicon, germanium and tin, preferably carbon, silicon or germanium, most preferably at least one of silicon or germanium. One or more other non-hydrogen atoms may also be present in the bridge, such as, e.g., Group 13 and 15 to 17 elements, non-limiting examples thereof including B, N, P, O, S, F and Cl.

[0021] In another embodiment, bridging group A is represented by R<sub>2</sub>C, R<sub>2</sub>C-CR<sub>2</sub>, R<sub>2</sub>Si, R<sub>2</sub>Ge, R<sub>3</sub>Si(R)Si, R<sub>3</sub>Si(R)C, R<sub>3</sub>Si(R)Ge and R<sub>3</sub>Ge(R)C, where the radicals R are independently selected from hydride, hydrocarbyl, substituted hydrocarbyl, disubstituted boron, disubstituted pnictogen (e.g., N or P), substituted chalcogen (e.g., O or S), and halogen. Illustrative, non-limiting examples of bridging group A include methylene, ethylene, ethylidene, propylidene, isopropylidene, diphenylmethylene, 1,2-dimethylethylene, 1,2-diphenylethylene, 1,1,2,2-tetramethylethylene, dimethylsilyl, diethylsilyl, methyl-ethylsilyl, trifluoromethylbutylsilyl, bis(trifluoromethyl)silyl, di(n-butyl)silyl, di(n-propyl)silyl, di(i-propyl)silyl, di(n-hexyl)silyl, dicyclohexylsilyl, diphenylsilyl, cyclohexylphenylsilyl, t-butylcyclohexylsilyl, di(t-

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[0027] In another embodiment, in Formula I, M is a Group 4 metal, preferably zirconium,  $L^A$  is 2,3,5-trimethylcyclopentadienyl group and  $L^B$  is an unsubstituted cyclopentadienyl group or a monomethyl cyclopentadienyl group and A is of the formula - $A'R^1R^2$ - wherein A' is Si or Ge and  $R^1$  and  $R^2$  are independently selected from  $C_1$ - $C_{20}$  hydrocarbyl groups. In another embodiment,  $R^1$  and  $R^2$  may form a 4 to 10 membered ring together with A. In preferred embodiments  $R^1$  and  $R^2$  are identical  $C_1$ - $C_6$  alkyl or  $C_6$ - $C_{14}$  aryl groups. In one embodiment, A is a di( $C_1$ - $C_4$  alkyl)silyl or a di( $C_1$ - $C_4$  alkyl)germyl radical.

[0028] In one embodiment, where the MIR of a polymer is to be controlled, according to the present invention, the catalyst composition that is based on a metallocene compound of Formula I where the maximum number of  $C_1$ - $C_2$  alkyl (e.g., methyl) groups attached to  $L^A$  and  $L^B$  (i.e., 8), usually affords the lowest MIR obtainable with a series of related catalysts (i.e., those having the same metal M, the same bridging group A and the same leaving group(s) Q). Conversely, the highest MIR can usually be obtained with a catalyst precursor compound of a given series that has the lowest number of  $C_1$ - $C_2$  alkyl groups attached to  $L^A$  and/or  $L^B$  (i.e., 3), in particular if one of the cyclopentadienyl rings  $L^A$  or  $L^B$  is unsubstituted. Metallocene catalyst precursor compounds having a total of 7, 6, 5 or 4  $C_1$ - $C_2$  alkyl groups attached to  $L^A$  and  $L^B$  afford intermediate values of MIR, a higher total number corresponding to a lower MIR within a given series of metallocene catalyst precursor compounds. Furthermore, a metallocene compound comprising an Si-containing bridging moiety usually affords a lower MIR (and also a lower melt strength) than its counterpart wherein the Si atom is replaced by a Ge atom.

[0029] In another embodiment of the present method for controlling the MIR, the catalyst system comprises a metallocene catalyst precursor compound including two bridged cyclopentadienyl ligands having a total of 3 to 8  $C_1$ - $C_2$  alkyl substituents. According to this method, the MIR of the polymer is increased by decreasing the total number of the  $C_1$ - $C_2$  alkyl substituents attached to  $L^A$  and  $L^B$ . Conversely, the MIR is decreased by increasing the total number of said  $C_1$ - $C_2$  alkyl substituents attached to  $L^A$  and  $L^B$ .

[0030] In another embodiment of this method, the metallocene compound contains a Group 4 metal, preferably zirconium, all of the  $C_1$ - $C_2$  alkyl substituents attached to  $L^A$  and/or  $L^B$  are methyl groups, and A contains Si or Ge.

[0031] In another embodiment of this method, bridging group A of Formula I is represented by the formula - $A'R^1R^2$ - wherein A' is Si or Ge and  $R^1$  and  $R^2$  are independently selected from  $C_1$ - $C_{20}$  hydrocarbyl groups. Alternatively,  $R^1$  and  $R^2$  may form a 4- to 10-

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alkylsulfonyl, alkyl-OCO etc. Illustrative, non-limiting examples of aryl radicals are phenyl, naphthyl, fluorenyl, chlorophenyl, dichlorophenyl, fluorophenyl, perfluorophenyl, hydroxyphenyl, anisyl, biphenyl, nitrophenyl, acetylphenyl, aminophenyl, pyridyl, pyridazyl, quinolyl, and the like. When carbon numbers are given herein for aryl radicals, ring  
5 heteroatoms are counted as carbon atoms. Unless otherwise stated, the above definition of the term "aryl" also applies to groups which comprise one or more aryl radicals. For example, the term "aryloxy" means an aryl ether radical wherein the term "aryl" is as defined above.

[0037] The terms "alkylaryl" and "arylalkyl" refer to groups composed of alkyl groups and aryl groups as defined above. Illustrative, non-limiting examples thereof are tolyl, xylyl  
10 (alkylaryl), benzyl and phenethyl (arylalkyl).

[0038] The term "hydrocarbyl" encompasses alkyl, alkenyl, aryl, arylalkyl and alkylaryl groups as defined above. Preferred hydrocarbyl groups comprise 1 to 20, more preferred 1 to 10, and most preferred 1 to 6 carbon atoms. Illustrative, non-limiting examples are methyl, ethyl, propyl and phenyl.

15 [0039] The term "halogen" refers to fluorine, chlorine, bromine and iodine.

#### Activators and Activation Methods for Catalyst Precursor Compounds

[0040] The catalyst precursor compounds for use in methods of the present invention are typically activated in various ways to yield, for example, compounds having a vacant  
20 coordination site that will coordinate, insert, and polymerize olefin(s). For the purposes of this specification and the appended claims, the term "activator" is defined to be any compound which can activate any one of the catalyst precursor compounds described above by converting a neutral catalyst precursor compound to a catalytically active catalyst compound, for example, a cation. Non-limiting examples of activators include alumoxanes, aluminum alkyls, ionizing  
25 activators, which may be neutral or ionic, and conventional-type activators.

#### A. Alumoxane and Aluminum Alkyl Activators

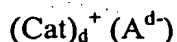
[0041] In one aspect, alumoxanes are utilized as activator (cocatalyst) in the catalyst composition for use in the methods of the invention. Alumoxanes are generally oligomeric,  
30 cyclic or acyclic, compounds containing -Al(R)-O- subunits (generally 6 to 40), where R is an alkyl group. Illustrative, non-limiting examples of alumoxanes include methylalumoxane (MAO), modified methylalumoxane (MMAO), ethylalumoxane and isobutylalumoxane.

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alkyl, aryl, arylhalide, alkoxy and halide radicals. Preferably, the three groups are independently selected from halogen, mono- or polycyclic (including halosubstituted) aryl, alkyl, alkoxy and alkenyl radicals and combinations thereof. Preferred are alkyl groups having 1 to 20 carbon atoms, alkenyl groups having 1 to 20 carbon atoms, alkoxy groups having 1 to 20 carbon atoms and aryl groups having 6 to 20 carbon atoms (including substituted aryl groups). More preferably, the three groups are independently selected from alkyl groups having 1 to 4 carbon groups, phenyl and naphthyl groups. Even more preferably, the three groups are halogenated, preferably fluorinated, aryl groups. Most preferably, the neutral stoichiometric activator is tris(perfluorophenyl) boron or tris(perfluoronaphthyl) boron.

**[0046]** Ionic stoichiometric activator compounds may contain an active proton, or some other cation associated with, but not coordinated to, or only loosely coordinated to, the remaining ion of the ionizing compound. Such compounds are described in European publications EP-A-0 570 982, EP-A-0 520 732, EP-A-0 495 375, EP-B1-0 500 944, EP-A-0 277 003 and EP-A-0 277 004, and U.S. Patent Nos. 5,153,157, 5,198,401, 5,066,741, 5,206,197, 5,241,025, 5,384,299 and 5,502,124 and pending U.S. Patent Application Serial No. 08/285,380, filed August 3, 1994.

**[0047]** In a preferred embodiment, the stoichiometric activators comprise a cation and an anion component, and may be represented by the following formula:



wherein

L is a neutral Lewis base;

H is hydrogen;

$(\text{Cat})^+$  is a Bronsted acid

$\text{A}^{d-}$  is a non-coordinating anion having the charge d-

d is an integer from 1 to 3.

**[0048]** The cation component,  $(\text{Cat})_d^+$  may include Bronsted acids such as protons or protonated Lewis bases or reducible Lewis acids capable of protonating or abstracting a moiety, such as an alkyl or aryl group, from the catalyst precursor compound, resulting in a cationic transition metal species.

**[0049]** The activating cation  $(\text{Cat})_d^+$  may be a Bronsted acid, capable of donating a proton to the catalyst precursor resulting in a transition metal cation, including ammonium,



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contacted with, vaporized with, bonded to, incorporated within, adsorbed or absorbed in, or on, a support or carrier.

#### A. Support Material

5 [0054] The support material may be any of the conventional support materials. Preferably the support material is a porous support material selected from, for example, talc, inorganic oxides, inorganic chlorides and combinations thereof. Other support materials include resinous support materials such as polystyrene, functionalized or crosslinked organic supports, such as polystyrene divinyl benzene polyolefins or polymeric compounds, zeolites, 10 clays, or any other organic or inorganic support material, or mixtures thereof.

[0055] The preferred support materials are inorganic oxides, more preferably those selected from oxides of Group 2, 3, 4, 5, 13 and 14 elements and combinations thereof. The more preferred supports include silica, fumed silica, alumina (see, e.g., WO 99/60033), silica-alumina and mixtures thereof. Other useful support materials include magnesia, titania, 15 zirconia, magnesium chloride (see, e.g., U.S. Patent No. 5,965,477), montmorillonite (see, e.g., European Patent EP-B1 0 511 665), phyllosilicate, zeolites, talc, clays (see, e.g., U.S. Patent No. 6,034,187) and the like. Also, combinations of these support materials may be used, for example, silica-chromium, silica-alumina, silica-titania and the like. Additional non-limiting examples of support materials include the porous acrylic polymers described in EP 0 767 184 20 B1; nanocomposites as described in PCT WO 99/47598; aerogels as described in WO 99/48605, spherulites as described in U.S. Patent No. 5,972,510; and polymeric beads as described in WO 99/50311. Another preferred support material is fumed silica available under the trade name Cabosil™ TS-610, available from Cabot Corporation. Fumed silica is typically a silica with particles 7 to 30 nanometers in size that has been treated with 25 dimethylsilyldichloride such that a majority of the surface hydroxyl groups are capped.

[0056] It is preferred that the support material, most preferably an inorganic oxide, has a surface area in the range of from 10 to 700 m<sup>2</sup>/g (square meters per gram), a pore volume in the range of from 0.1 to 4.0 cm<sup>3</sup>/g and an average particle size in the range of from 5 to 500 μm (micrometers). More preferably, the surface area of the support material is from 50 to 500 30 m<sup>2</sup>/g, the pore volume is from 0.5 to 3.5 cm<sup>3</sup>/g and the average particle size is from 10 to 200 μm. Most preferably the surface area of the support material is from 100 to 400 m<sup>2</sup>/g, the pore

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alumoxane and adding more methylalumoxane; U.S. Patent Nos. 5,756,416 and 6,028,151 discuss a catalyst composition of an alumoxane impregnated support and a metallocene and a bulky aluminum alkyl and methylalumoxane; EP-B1-0 662 979 discusses the use of a metallocene with a catalyst support of silica reacted with alumoxane; PCT WO 96/16092  
5 relates to a heated support treated with alumoxane and washing to remove unfixed alumoxane; U.S. Patent Nos. 4,912,075, 4,937,301, 5,008,228, 5,086,025, 5,147,949, 4,871,705, 5,229,478, 4,935,397, 4,937,217 and 5,057,475, and PCT WO 94/26793 all are directed to adding a metallocene to a supported activator; U.S. Patent No. 5,902,766 relates to a supported activator having a specified distribution of alumoxane on the silica particles; U.S. Patent No. 5,468,702  
10 relates to aging a supported activator and adding a metallocene; U.S. Patent No. 5,968,864 discusses treating a solid with alumoxane and introducing a metallocene; EP 0 747 430 A1 relates to a process using a metallocene on a supported methylalumoxane and trimethylaluminum; EP 0 969 019 A1 discusses the use of a metallocene and a supported activator; EP-B2-0 170 059 relates to a polymerization process using a metallocene and a  
15 organoaluminum compound, which is formed by reacting aluminum trialkyl with a water containing support; U.S. Patent No. 5,212,232 discusses the use of a supported alumoxane and a metallocene for producing styrene based polymers; U.S. Patent No. 5,026,797 discusses a polymerization process using a solid component of a zirconium compound and a water-insoluble porous inorganic oxide preliminarily treated with alumoxane; U.S. Patent No.  
20 5,910,463 relates to a process for preparing a catalyst support by combining a dehydrated support material, an alumoxane and a polyfunctional organic crosslinker; U.S. Patent Nos. 5,332,706, 5,473,028, 5,602,067 and 5,420,220 discuss a process for making a supported activator where the volume of alumoxane solution is less than the pore volume of the support material; WO 98/02246 discusses silica treated with a solution containing a source of  
25 aluminum and a metallocene; WO 99/03580 relates to the use of a supported alumoxane and a metallocene; EP-A1-0 953 581 discloses a heterogeneous catalytic system of a supported alumoxane and a metallocene; U.S. Patent No. 5,015,749 discusses a process for preparing a polyhydrocarbyl-alumoxane using a porous organic or inorganic imbibitor material; U.S. Patent  
Nos. 5,446,001 and 5,534,474 relate to a process for preparing one or more alkylaluminumoxanes  
30 immobilized on a solid, particulate inert support; and EP-A1-0 819 706 relates to a process for preparing a solid silica treated with alumoxane. Also, the following articles, which disclose useful supported activators and methods for their preparation, may be referred to: W.

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[0066] Other examples of supporting an activator are described in U.S. Patent No. 5,427,991, where supported non-coordinating anions derived from tris(perfluoro-phenyl) boron are described; U.S. Patent No. 5,643,847 discusses the reaction of Group 13 Lewis acid compounds with metal oxides such as silica and illustrates the reaction of tris(perfluorophenyl) boron with silanol groups (the hydroxyl groups of silica) resulting in bound anions capable of protonating transition metal organometallic catalyst compounds to form catalytically active cations counter-balanced by the bound anions; immobilized Group IIIA Lewis acid catalysts suitable for carbocationic polymerizations are described in U.S. Patent No. 5,288,677; and James C.W. Chien, Jour. Poly. Sci.: Pt A: Poly. Chem., Vol. 29, 1603 - 1607 (1991), describes the olefin polymerization utility of methylalumoxane (MAO) reacted with silica ( $\text{SiO}_2$ ) and metallocenes and describes a covalent bonding of the aluminum atom to the silica through an oxygen atom of the surface hydroxyl groups of the silica.

[0067] In a preferred embodiment, a supported activator is formed by preparing in an agitated, and temperature and pressure controlled vessel a solution of the activator and a suitable solvent, then adding the support material at temperatures from  $0^\circ\text{C}$  to  $100^\circ\text{C}$ , contacting the support with the activator solution for up to 24 hours, then using a combination of heat and pressure to remove the solvent to produce a free flowing powder. Temperatures can range from  $40$  to  $120^\circ\text{C}$  and pressures from 5 psia to 20 psia (34.5 to 138kPa). An inert gas sweep can also be used to assist in removing solvent. Alternate orders of addition, such as slurring the support material in an appropriate solvent then adding the activator, can be used.

#### Polymerization Process

[0068] The methods of the present invention described above are suitable for use in any prepolymerization and/or polymerization process over a wide range of temperatures and pressures. For example, the temperatures may be in the range of from  $-60^\circ\text{C}$  to  $280^\circ\text{C}$ , preferably from  $50^\circ\text{C}$  to  $200^\circ\text{C}$ , and the pressures employed may be in the range from 1 atmosphere to 500 atmospheres or higher.

[0069] Polymerization processes include solution, gas phase, slurry phase and a high pressure processes and combinations thereof. Preferred is a gas phase polymerization of ethylene and one or more additional olefins.

[0070] In one embodiment, the process is a solution, high pressure, slurry or gas phase polymerization process of ethylene and one or more olefin monomers having from 3 to 30

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contemplated by the invention include those described in U.S. Patent Nos. 5,627,242, 5,665,818 and 5,677,375, and European publications EP-A- 0 794 200 EP-B1-0 649 992, EP-A- 0 802 202 and EP-B- 634 421.

[0077] The methods of the present invention may also be applied for slurry polymerization processes. These processes generally use pressures in the range of from 1 to 50 atmospheres and even greater and temperatures in the range from 0°C to 120°C. In a slurry polymerization, a suspension of solid, particulate polymer is formed in a liquid polymerization diluent medium to which ethylene and comonomers and often hydrogen along with catalyst are added. The suspension including diluent is intermittently or continuously removed from the reactor where the volatile components are separated from the polymer and recycled, optionally after a distillation, to the reactor. The liquid diluent employed in the polymerization medium is typically an alkane having from 3 to 7 carbon atoms, preferably a branched alkane. The medium employed should be liquid under the conditions of polymerization and relatively inert. When a propane medium is used the process must be operated above the reaction diluent critical temperature and pressure. Preferably, a hexane or an isobutane medium is employed.

[0078] A preferred slurry polymerization technique is referred to as a particle form polymerization, or a slurry process where the temperature is kept below the temperature at which the polymer goes into solution. Such technique is well known in the art, and described in, for instance, U.S. Patent No. 3,248,179. Other slurry processes include those employing a loop reactor and those utilizing a plurality of stirred reactors in series, parallel, or combinations thereof. Non-limiting examples of slurry processes include continuous loop or stirred tank processes. Also, other examples of slurry processes are described in U.S. Patent No. 4,613,484 and 5,986,021.

[0079] Examples of solution processes to which the methods of the present invention can be applied are described in U.S. Patent Nos. 4,271,060, 5,001,205, 5,236,998, 5,589,555 and 5,977,251 and PCT WO 99/32525 and PCT WO 99/40130.

#### Polymer Products

[0080] The polymers produced by using the methods of the present invention can be used in a wide variety of products and end-use applications. These polymers include linear low density polyethylene, elastomers, plastomers, high density polyethylenes, medium density polyethylenes and low density polyethylenes.

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oriented films, snack packaging, heavy duty bags, grocery sacks, baked and frozen food packaging, medical packaging, industrial liners, membranes, etc. in food-contact and non-food contact applications. Fibers include those made by melt spinning, solution spinning and melt blown fiber operations for use in woven or non-woven form to make filters, diaper fabrics, medical garments, geotextiles, etc. Extruded articles include medical tubing, wire and cable coatings, pipe, geomembranes, and pond liners. Molded articles include single and multi-layered constructions in the form of bottles, tanks, large hollow articles, rigid food containers and toys, etc.

[0087] The following examples further illustrate the invention.

#### 10 EXAMPLES

##### Testing Procedures:

[0088] **Melt Strength Test Method A** - Melt strength is measured with an Instron capillary rheometer in conjunction with the Goettfert Rheotens melt strength apparatus. A polymer melt strand extruded from the capillary die is gripped between two counter-rotating wheels on the apparatus. The take-up speed is increased at a constant acceleration of 24 mm/sec<sup>2</sup>, which is controlled by the Acceleration Programmer (Model 45917, at a setting of 12). The maximum pulling force (in the unit of cN) achieved before the strand breaks or starts to show draw-resonance is determined as the melt strength.

[0089] The temperature of the rheometer is set at 190°C. The barrel has a diameter of 0.375" (9.525 mm). The capillary die has a length of one inch (25.4 mm) and a diameter of 0.06" (1.5 mm). The polymer melt is extruded from the die at a piston speed of 3 inch/min (1.27 mm/sec). The apparent shear rate for the melt in the die is, therefore, 260 sec<sup>-1</sup> and the speed at die exit is 49.6 mm/sec. The distance between the die exit and the wheel contact point should be 3.94 inches (100 mm).

25 [0090] **Method Strength Test Method B** - Melt strength is measured with a capillary rheometer (RHEO-TESTER 1000) in conjunction with the Goettfert Rheotens melt strength apparatus (RHEOTENS 71.97). A polymer melt strand extruded from the capillary die is gripped between two counter-rotating wheels on the apparatus. The take-up speed is increased at a constant acceleration of 12 mm/sec<sup>2</sup>, which is controlled by the WinRHEO program provided by Goettfert. The maximum pulling force (in the unit of cN) achieved before the strand breaks or starts to show draw-resonance is determined as the melt strength.

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reaction mixture was extracted with pentane (2 x 50 ml), filtered and to the extracts was added 30 ml diethyl ether. The ligand was deprotonated with n-BuLi (25 ml, 2.5 M). The dilithio salt was collected on a medium glass frit and washed with pentane (3.6 g). It was dissolved in diethyl ether (100 ml) and reacted with ZrCl<sub>4</sub> (2.9 g). The reaction mixture was filtered after 2 hours and the filtrate reduced and pentane added. The filtrate was cooled to -35° C and the next day product (title compound) was collected as a white solid (1.3 g).

[0098] The above product (0.73 g) was weighed into a beaker with a stir bar and reacted with MAO (53.5 g, 30 wt% in toluene). Additional toluene was added (53.5 g). The reaction mixture was homogeneous after 10 min. and the stirring was stopped. Incremental amounts of silica gel (40 g) were added and mixed with a spatula. The resulting mud was dried *in vacuo* until free-flowing and transferred into a bomb for screening purposes.

#### Synthesis of Metallocenes Nos. 2-28

[0099] Metallocenes Nos. 2-28, were synthesized in a similar manner as utilized to prepare Metallocene No. 1. Metallocenes Nos. 2-28 were synthesized and then reacted with MAO and supported on silica to prepare a catalyst composition for use in the methods of the present invention. Table 1 below lists the metallocenes catalyst compounds prepared. Table 2 below summarizes the reagents used for the preparation of the corresponding catalyst systems.

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TABLE 2

## Reagents for Preparation of Catalyst Composition

Composition	Metallocene/g	30% MAO, g	Toluene, g	Silica, g	Silica Type
1	0.74	53.5	53.5	40	D
2	0.75	53.5	53.5	40	D
3	0.73	53.5	53.5	40	D
4	1.62	108.1	108.1	80	D
5	1.18	53.5	54	40	D
6	0.45	34	34	25	Cr
7	0.39	53.5	53.5	40	D
8	0.71	53.5	53.5	40	D
9	0.48	33.5	33.5	25	D
10	0.51	34	34	25	Cr
11	0.79	53.5	53.5	40	D
12	0.52	34.5	34.5	25	D
13	0.6	34	34	25	Cr
14	0.62	34	34	25	Cr
15	0.42	25	25	26	D
16	0.45	25	25	26	D
17	0.6	26	26	25	D
18	0.6	24	24	25	D
19	0.51	25.8	26	25	D
20	0.78	31.9	32.7	25	D
21	0.73	32.3	33.2	25.4	D
22	1.15	51.0	52.3	40	D
23	1.13	51.0	52.3	40	D
24	1.19	51.0	52.3	40	D
25	0.65	31.4	33.1	25	D
26	0.77	37.6	39.7	30	D
27	0.84	37.6	39.7	30	D
28	0.75	35.7	37.8	28.6	D

D = Davison 948, Cr = Crosfield ES-70

5 Davison 948 is available from Grace Davison, Baltimore MD. Crosfield ES-70 is available from Ineos, United Kingdom.

TABLE 3  
Polymerization Conditions and Polymer Properties

Composition	1	2	3	4	5	6	15
Temp., F	175	165	175	175	175	175	175
Pressure, psig	300	300	300	300	300	300	300
C <sub>2</sub> mol %	35	25.1	35.2	34.5	35	35	35
H <sub>2</sub> mol ppm	106	94	313	306	659	771	435
H <sub>2</sub> /C <sub>2</sub> ratio	3	3.7	8.9	8.9	18.9	22	12.4
C <sub>6</sub> mol %	0.87	0.3	0.52	0.46	0.47	0.33	0.35
C <sub>6</sub> /C <sub>2</sub> ratio	0.025	0.012	0.015	0.013	0.013	0.009	0.01
Bed Weight, g	1930	1835	1818	1983	2399	1890	1889
Residence Time, hr	4.8	4.6	3.9	3.2	8.2	3.9	4.3
Gas Velocity	1.57	1.77	1.56	1.56	1.58	1.61	1.6
Prod. Rate g/hr	400	399	465	611	293	481	440
Bulk Density	0.388	0.458	0.49	na	na	0.502	0.4365
Productivity g/g	3458	1532	2233	2640	271	1618	868
MI, dg/min	1.7	1.31	2.17	2.1	2.4	0.81	3.1
MIR	31.7	37	40	44	51.1	56	30.2
MS, cN	7.4 (6.5)	8.4	4.9	7.6	4.2	11.2 (10.8)	8.1
MS Method	A (B)	A	A	A	A	A (B)	A
Density, g/cm <sup>3</sup>	0.9193	0.9196	0.9233	0.9183	0.9185	0.9153	0.9195
M <sub>w</sub>	109,000	140,000	113,600	149,700	98,000	-	-
M <sub>w</sub> /M <sub>n</sub>	5.8	6.5	7.5	7.3	5.0	-	-



TABLE 3 (continued)

Composition	7	8	9	10	16	17	18
Temp., F	175	175	175	175	175	175	175
Pressure, psig	300	300	300	300	300	300	300
C <sub>2</sub> mol%	35	35.1	35	34.9	35.1	35.1	35
H <sub>2</sub> mol ppm	1024	904	686	720	436	384	323
H <sub>2</sub> /C <sub>2</sub> ratio	29.3	25.7	19.6	20.6	12.4	10.9	9.2
C <sub>6</sub> mol %	0.33	0.63	0.34	0.31	0.32	0.99	0.58
C <sub>6</sub> /C <sub>2</sub> ratio	0.009	0.018	0.01	0.009	0.009	0.028	0.017
Bed Weight, g	1874	1868	1918	1881	1899	1947	1926
Residence Time, hr	2.6	8.1	4.4	6	4.5	5	4.8
Gas Velocity	1.6	1.6	1.59	1.57	1.59	1.58	1.61
Prod. Rate g/hr	713	231	440	315	418	391	404
Bulk Density	0.4798	na	0.4503	0.486	na	na	0.3815
Productivity g/g	959	444	1267	357	683	750	946
MI, dg/min	1.6	0.7	0.54	0.4	2.1	0.64	1.3
MIR	83	90	174	123	33.3	77	56.2
MS, cN	5.5	5.8	5.8	9.1	11.8	8.9 (8.3)	8
MS Method	A	A	A	A	B	A (B)	B
Density, g/cm <sup>3</sup>	0.9232	0.9199	0.9235	0.9184	0.9195	0.9189	0.9196

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[0102] A comparison of the results of Table 3 shows that catalyst compositions derived from metallocene catalyst precursor compounds wherein one of the cyclopentadienyl ligands is 2,3,5-trisubstituted and the other one is unsubstituted (or not fully substituted, respectively) afford ethylene/1-hexene copolymers having a melt strength which in most cases is significantly higher than that achieved with the remaining catalyst compositions tested, irrespective of the type of the bridging group.

[0103] Furthermore, as can be seen, for example, from a comparison of the MIR data obtained with compositions 1 to 5 (derived from metallocene catalyst precursor compounds having one tetramethylcyclopentadienyl ligand and one cyclopentadienyl ligand substituted by 4, 3, 2, 1 and 0 methyl groups, respectively), the MIR values of the ethylene copolymers increase with decreasing substitution of the second cyclopentadienyl ligand.

[0104] While the present invention has been described and illustrated by reference to particular embodiments, it will be appreciated by those of ordinary skill in the art, that the invention lends itself to many different variations not illustrated herein. For these reasons, then, reference should be made solely to the appended claims for purposes of determining the true scope of the present invention.

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8. The method of claim 1, wherein the bridging group is represented by the formula  $-AR^1R^2-$  wherein A' is selected from Si and Ge, and  $R^1$  and  $R^2$  are independently selected from  $C_1$ - $C_{20}$  hydrocarbonyl groups, and wherein  $R^1$  and  $R^2$  together with A may form a 4 to 10 membered ring.

9. The method of claim 1 wherein the metal atom is also bound to at least one anionic leaving group selected from the group consisting of hydrogen, halogen, amino, alkyl, alkoxy, aryl, aryloxy, alkenyl, arylalkyl, alkylaryl, arylalkenyl groups and combinations thereof.

10. The method of claim 1, wherein the activator is an alumoxane.

11. The method of claim 1, wherein the at least one olefin comonomers comprise an olefin having 3 to 12 carbon atoms.

12. The method of claim 1, wherein the melt strength is increased and wherein ethylene and 1-hexene are contacted with a catalyst composition comprising the product of (a) a zirconocene compound comprising a 2,3,5-trimethylcyclopentadienyl ligand bridged to an unsubstituted cyclopentadienyl ligand and (b) methyl alumoxane.

13. The method of claim 1, wherein the method is applied to a gas phase or a slurry phase polymerization process.

14. The method of claim 1, wherein the polymer has a density of at least  $0.900 \text{ g/cm}^3$ .

15. The method of claim 1, wherein the melt strength is kept above 6.0 cN.

16. The method of claim 1, wherein the melt strength is kept above 8.0 cN.

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25. The method of claim 17, wherein the at least one olefin comonomers comprise an olefin having 3 to 12 carbon atoms.

26. The method of claim 17, wherein ethylene and 1-hexene are contacted with the catalyst system, and the metallocene compound comprises a Group 4 metal, the activator comprises methyl alumoxane, and all of the C<sub>1</sub>-C<sub>2</sub> alkyl groups are methyl groups.

27. The method of claim 17, wherein the method is applied to a gas phase or a slurry phase polymerization process.

28. The method of claim 17, wherein the polymer has a density greater than 0.900g/cm<sup>3</sup>.

29. The method of claim 17, wherein the Melt Index Ratio greater than 20.

30. The method of claim 17, wherein the polymer has a molecular weight distribution of from 3 to 10.

31. The method of claim 17, wherein the polymer has a Melt Index of greater than 0.01.